

Membrane and use thereof

The invention relates to membranes, in particular open pore membranes that can be used for gas separation, ultra filtration or in particular for medical purposes such as for
5 haemodialysis, blood filtration, haemodiafiltration, plasma phoresis or immunotherapy.

A method for manufacturing polymer hollow fibre membranes is known from DE-A-19 520 188 in which a molten polymer for forming the hollow fibre membranes is lead
10 through an extrusion apparatus, wherein the polymer, under pressure before entry into an extrusion tool that shapes the molten mass, belonging to the extrusion apparatus, is charged with gas, and wherein as a result of the drop in pressure occurring to a pre-determined extent when the polymer exits the extrusion apparatus and the consequently occurring expansion of the gas in the polymer, a porous hollow fibre
15 membrane forms. The open porosity and pore size obtained using this method do not produce satisfactory separation results as the open porosity percentage is too low and the pores are too large. The pore size determines the separating action and the degree of open porosity the efficiency of the membrane.

20 WO 91/08 243 describes a method for manufacturing open cell polyurethane foam by mixing a di-isocyanate, a hydrogen donor, at least one surface active material, at least one catalyst and a blowing agent, which is advantageously carbon dioxide, pressurising the mixture in the mixing area in order to keep the blowing agent in a liquid state at ambient temperature, ejection of the mixture into an environment at atmospheric
25 pressure with momentary vaporisation of the blowing agent and curing of the resulting foam at ambient temperature. This method has the same disadvantages as that described hereinabove.

The object of the invention is thus to provide open pore membranes, in particular surface fibre membranes or hollow fibre membranes, that have as high a degree of open porosity as possible as well as open pores that are as small and regular in size as possible.

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According to the invention, this object is solved with a membrane that can be manufactured in that a polymer or polymer mix is shaped as desired, the polymer or polymer mix is charged with a gas at above atmospheric pressure before or after shaping, and then the gas-charged polymer is foamed at a temperature above the glass
10 transition temperature of the polymer/gas mixture, and lastly the foam structure is stabilised by cooling. According to the invention, this method is characterised in that the gas-charged polymer is foamed using an amount of 0.05 to 4.0% by weight of a fluid that dissolves or swells the polymer. This is a liquid or a gas, preferably an organic liquid. Liquids that dissolve the polymer are preferred.

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Until now it was usual to process foams with the type of method described, using solvent-free polymer. It was unexpected that in the presence of a small amount of a fluid that dissolves or swells the polymer, which will hereinafter also be referred to as a solvent, the pore structure is improved in terms of the object of the invention, that is
20 to say a high degree of open porosity and uniformly small pore size is obtained.

Evaluation of the open porosity can be carried out in the following ways:

a) With the aid of scanning electron microscope pictures:

With this the sample is broken in liquid nitrogen, and the cleavages analysed.
25 If the scanning electron microscope pictures show apertures or fractures in the cell walls, this indicates open porosity.

b) With the aid of flow measurements:

With this, a sample is fixed into an appropriate measuring apparatus, wherein the ends of the membrane are respectively broken in liquid nitrogen. The sample is embedded in a resin so that the top surfaces and lateral surfaces are completely covered
5 over. A gas or a liquid, which can be pressurised, is applied to an open end. By measuring the flow volume of gas or liquid, the open porosity can be characterised. The open porosity is indicated by a significantly higher flow compared to closed pore samples.

10 c) By measuring the capillary elevation:

With this, a sample is fixed into an appropriate measuring installation, wherein the ends of the polymer sample are respectively broken in liquid nitrogen. The end of the fixed sample is immersed approximately 2 to 3 mm in a liquid. After an appropriate time the elevation of the liquid level in the membrane is measured. Using
15 changes in weight as well as elevation, the open porosity can be characterised. Closed pore samples absorb no liquid, and the elevation cannot be measured.

For manufacturing the open pore membranes according to the invention, there are three types of method to be considered that are known per se. The first type of method
20 is the so-called pressurised cell method, in which the polymer or the polymer mix is firstly shaped as required and then, at atmospheric pressure and at a temperature below the glass transition temperature of the polymer/gas mixture, is charged with a gas. The temperature is then raised above the glass transition temperature of the polymer/gas mixture such as by immersion into a hot bath, and the gas is then driven out of the
25 blank, whereby the desired open porosity is produced.

The second type of method is the so-called autoclave method, in which the charging of

the polymer or of the polymer mix with the gas takes place at a temperature above the glass transition temperature of the polymer/gas mixture, and foaming is initiated by a spontaneous increase in pressure. In contrast to the pressurised cell method, in which the gas-charged polymer is normally put into a hot bath in order to obtain the
5 temperature above the glass transition temperature, with the autoclave method, such heating is unnecessary, as the polymer is already at the necessary temperature above the glass transition temperature when charged with the gas.

The third type of method is the so-called extrusion method, in which a molten mass of
10 polymer or polymer mix is charged with the gas in a shaping extrusion tool. On leaving the extrusion tool, and the drop in pressure caused by this, foaming occurs.

The pressurised cell method is currently preferred.

15 The liquid dissolving or swelling the polymer can be introduced into the solvent-free polymer or polymer mix by infiltration. Infiltration can take place as follows. The solvent-free polymer (total residue $<0.01\%$) is treated in a flow reactor with a stream of gas enriched with solvent. With this, the solvent concentration in the polymer is increased. With the aid of temperature, gas stream, dwell time, and solvent
20 concentration in the gas stream, different solvent concentrations can be put into the polymer. Treatment is also conceivable in which the polymer is situated in a vapour chamber saturated with solvent. It is preferable, however, as it is technically more simple, to leave the dissolving or swelling liquid as a residue in the polymer during manufacture of the polymer or polymer mix. Optionally, both kinds of method can be
25 employed together, for example, when during the manufacture of the polymer too little residue remains in the polymer or polymer mix, so supplementing by infiltration has to take place.

The content of liquid that dissolves or swells the polymer necessary for the result desired depends on the respective polymers and solvents used. Because of the objects described hereinabove, however, it is a simple matter for the skilled person to
5 determine, using a few routine experiments, what solvent content is optimum for a certain polymer and a certain solvent, and with established parameters such as gassing pressure when charging the polymer with the gas, and foaming temperature.

Regardless of the type of method, different charging gases such as air, noble gases,
10 nitrogen, tetrafluoroethylene, fluoroform, hexafluoroethane or mixtures of these can be used, as is known from the prior art. Carbon dioxide is, however, preferably used as the charging gas. Advantageously, the polymer or the polymer mix is saturated under pressure with the charging gas.

15 The pore structure obtained by foaming must be stabilised by cooling the polymer blank. In order to prevent later changes in the pore structure during cooling, it is advantageous to stabilise the polymer blank after foaming by chilling, preferably to a temperature below the glass transition temperature of the polymer.

20 The foaming temperature depends on the specifically used polymer. Normally, the foaming temperature is in the range of 100 to 200°C, but the subject-matter of the invention is not limited to this temperature range. The liquids, preferably organic, that dissolve or swell the polymer, that were used in the previous method, also depend on the polymers used and their solubility. Advantageous examples of these organic
25 liquids are tetrahydrofuran, 1,2-dichloroethane and 1-methyl-2-pyrrolidone

Amorphous plastics, partly crystalline plastics, liquid crystal plastics, duroplastics,

elastic rubber plastics or mixtures of these can be considered as polymers in the method described above. Advantageous examples of polymers are polysulfone, polyethersulfone, polyetherketone, polyaramide, polycarbonate, cellulose and cellulose derivatives such as cellulose ester or cellulose ether.

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As described hereinabove, it is particularly advantageous to manufacture the membranes according to the invention in the form of a surface or hollow fibre membrane. Such membranes can be used for gas separation, preferably also for medicinal purposes such as haemodialysis, blood filtration, haemodiafiltration, plasma
10 phoresis or immunotherapy, or also for non-medical purposes such as for micro or ultrafiltration. According to the purpose for which they are used, the membranes can be symmetrical or asymmetrical, wherein asymmetrical means there is a larger pore size with respect to one of the two surfaces than with respect to the other surface, or even having closed pores or a closed skin on one surface.

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The following examples serve to explain the invention in more detail.

Examples

20 The following examples are implemented in every respect in the manner described hereinafter, wherein only the polymers, solvents and foaming temperatures have been changed.

The given polymer was dissolved in a quantity of 20% by weight in the solvent
25 described hereinafter. This solution was spread with a spreading blade to a thickness of 0.50 mm onto a glass plate. The polymer film was dried in a nitrogen gas stream.

In order to adjust the solvent residue concentration additional drying took place in a vacuum drying chamber. The solvent residue concentration was varied.

5 The solvent residue-containing polymer film thus obtained was saturated with carbon dioxide at 50 bar and at approximately 20 to 25° for 2 hours in a pressurised cell. After releasing the pressure and opening the pressurised cell, the polymer film was immersed for 10 to 60 seconds in a hot bath at the foaming temperature described hereinafter. After foaming, the polymer film was chilled to approximately 20° in a mixture of ethanol and water.

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Example 1

In this example, a polysulfone (Udel P-3500, Amoko) was used as the polymer with solvent residue concentrations of tetrahydrofuran. A foaming temperature of 165°C was used. Open cell membranes were respectively obtained with a solvent residue content (tetrahydrofuran) of 1.23% by weight, 0.94% by weight, 0.68% by weight 0.38% by weight, 0.33% by weight, 0.24% by weight, 0.10% by weight and 0.07% by weight. When the solvent residue content was reduced to 0.01%, closed cell membranes were obtained instead.

20 Example 2

Example 1 was repeated using 1,2 dichloroethane. With a solvent residue content of 3.4% by weight and a foaming temperature of 165°C, an open cell membrane was obtained. With 8.0% by weight solvent residue content, however, only closed cell membranes were obtained.

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Example 3

In this example, instead of polysulfone, a polyethersulfone (5200-P, ICI) was used as the polymer. As the organic liquid or solvent, 1-methyl-2-pyrrolidone was used. The foaming temperature was approximately 185°C. Open cell membranes were obtained with a solvent residue content of 4.39% by weight, 4.3% by weight, 3.54% by weight, 5 3.47% by weight and 2.48% by weight. With a solvent residue content of 5.66% by weight, however, the membranes were closed-celled.

Example 4

In this example, a polycarbonate (BPZ-PC S 24/4, Bayer) was used as the polymer in 10 combination with tetrahydrofuran as the solvent and a foaming temperature of 140°C. With solvent residue contents of 0.50% by weight, 0.36% by weight and 0.31% by weight, open cell membranes were produced.